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Winter–summer differences of carbon dioxide and oxygen in the Weddell Sea surface layer

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Abstract

Mid-winter total inorganic carbon (TCO_2) and oxygen measurements are presented for the central fully ice-covered Weddell Sea. Lateral variations of these properties in the surface layer of the central Weddell Sea were small but significant. These variations were caused by vertical transport of Warm Deep Water into the surface layer and air–sea exchange before the ice cover. Oxygen saturation in the surface layer of the central Weddell Sea was near 82%, whereas in the eastern shelf area this was 89%. Surprisingly, $p\text{CO}_2$, as calculated under the assumption of (reported) conservativeness of alkalinity, was also found to be below saturation (86–93%). This was not expected since ongoing Warm Deep Water entrainment into the surface layer tends to increase the $p\text{CO}_2$. Rapid cooling and subsequent ice formation during the previous autumn, however, might have brought about a sufficiently low undersaturation of CO_2 , that as to the point of sampling had not yet been replenished through Warm Deep Water entrainment.

In the ensuing early summer the measurements were repeated. In the shelf area and the central Weddell Sea, where the ice-cover had almost disappeared, photosynthesis had caused a decrease of $p\text{CO}_2$ and an increase of oxygen compared to the previous winter. In between these two regions there was an area with significant ice-cover where essentially winter conditions prevailed.

Based on the summer–winter difference a (late-winter) entrainment rate of Warm Deep Water into the surface layer of 4–5 m/month was calculated. A complete surface water balance, including entrainment, biological activity and air–sea exchange, showed that between the winter and summer cruises CO_2 and oxygen had both been absorbed from the atmosphere. The TCO_2 increase due to entrainment of Warm Deep Water was partly countered by (autumn) cooling, and partly through biological drawdown. Part of the CO_2 removed through biological activity sinks down the water column as organic material and is remineralised at depth. It is well-known that bottom water formation constitutes a sink for atmospheric CO_2 . However, whether the Weddell Sea as a whole is a sink for CO_2 depends on the ratio of two counteracting processes, i.e. entrainment, which increases CO_2 in the surface and the biological pump, which decreases it. As deep water is not only entrained into the surface, but also conveyed out of the Weddell Sea, the relative importances of these (CO_2 -enriched) deep water transports are important as well.

1. Introduction

South of the Antarctic Circumpolar Current, the Weddell Gyre is the most pronounced circulation structure of the Antarctic Ocean. The main portion of bottom water formation in the Antarctic Ocean occurs in the Weddell basin. Source waters of the Weddell Sea Bottom Water are the waters on the southern and western continental shelves and the top stratum of the Warm Deep Water of the Weddell Sea (Mosby, 1934; Gill, 1973; Foster and Carmack, 1976). Shelf water is formed from offshore surface water, which is further cooled and enriched in salt by ice formation (although freshening by glacial melt water and precipitation tend to counteract this to a certain extent). The other major component of bottom water is the Warm Deep Water. Latter provides sufficient salt to reach the density required to form bottom water. Warm Deep Water is an expansion of the Circumpolar Deep Water, by definition spatially restricted to the Weddell Gyre. The oxygen-poor Warm Deep Water is mixed in considerable quantities into the offshore surface layer as can be concluded from the substantial undersaturation of oxygen under the wintertime pack-ice (Weiss et al., 1979; Gordon et al., 1984).

High-latitude areas have since long perked interest in studies of greenhouse gases in the oceans (e.g. Deacon, 1940; Anderson and Jones, 1991), among which carbon dioxide (CO_2) is the most important. On solubility grounds, these areas are potentially strong in sequestering these gases. The role of the Antarctic Ocean in the greenhouse debate has not yet been definitely settled. One reason is that CO_2 data are still scanty, especially in winter and concerning the seasonal cycle. In addition, the importance of upwelling of Warm Deep Water with its high CO_2 concentration is not clear-cut. Therefore, it is our aim to investigate the variability of CO_2 in the surface water of the Weddell Sea, and account for the role of the Warm Deep Water. For the first time CO_2 and oxygen data are presented for the Weddell Sea interior which represent midwinter conditions of the offshore surface water (the Winter Water) and the surface water from the eastern shelves. This data set is supplemented by extensive summer data from the same region.

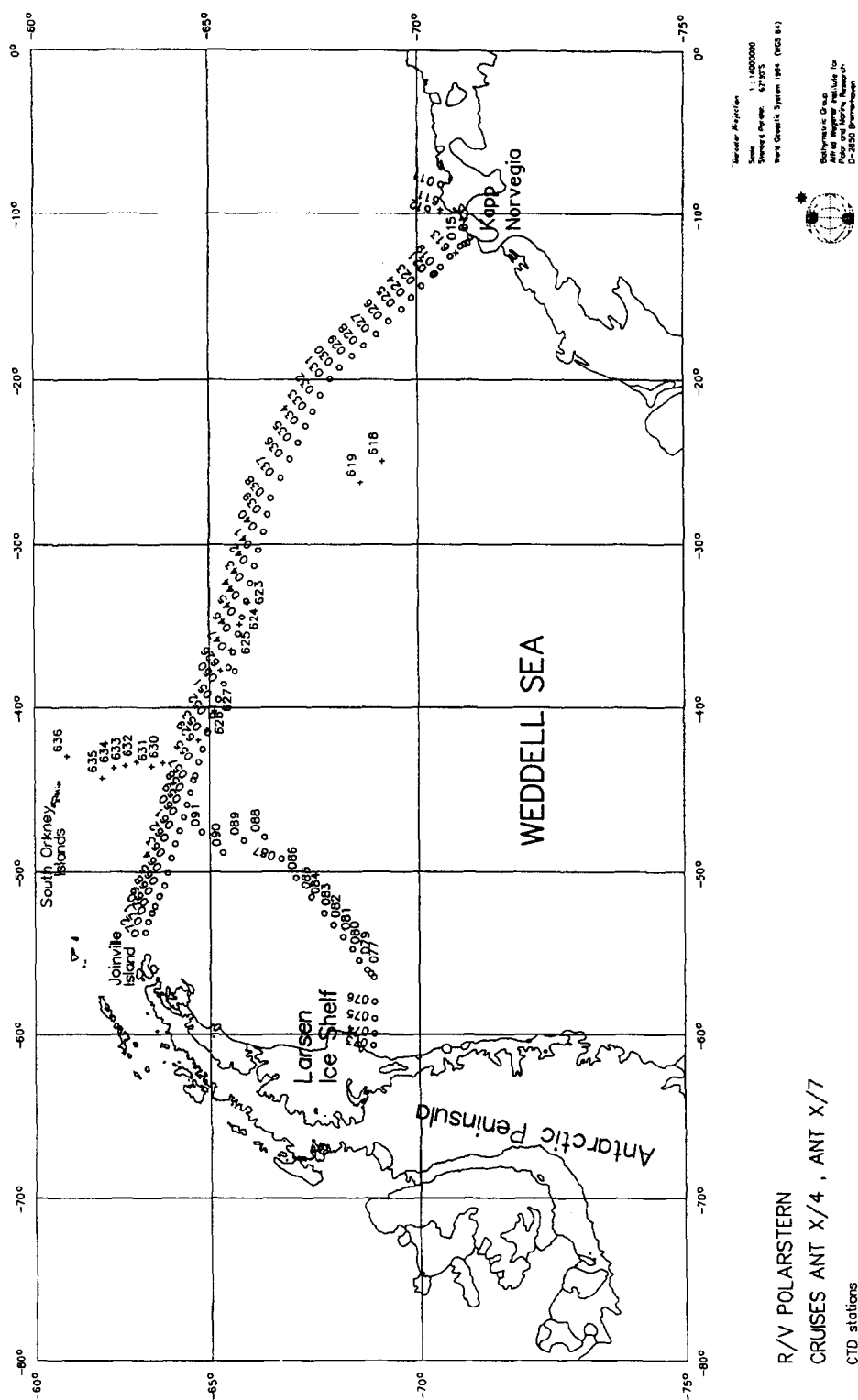
Much effort has been put in investigating the

Weddell circulation. Since 1989 a project has been running at the Alfred-Wegener-Institut studying the Weddell Gyre with recurrent CTD-transects and mooring arrays. This has provided a more detailed picture of the large-scale circulation and transports (Fahrbach et al., 1994a, b). With the winter and summer cruises that are reported here, the project was extended to encompass the investigation on the role of the Weddell Sea and adjacent regions in the carbon cycle.

2. Sampling and methods

Data are presented from the cruises ANT X/4 in June/July 1992 (Lemke, 1994) and ANT X/7 in December 1992/January 1993 (Fahrbach, 1994) of FS *Polarstern*. At all hydrographic stations (Fig. 1) water samples were collected from a 24-place rosette sampler. Temperature was obtained from the CTD-probe; accuracy was set by shore-based calibration and amounted to 3 mK. Salinity, with accuracy 0.003, was standardised using an Autosal 8400A salinometer. All salinities in this paper are given on the Practical Salinity Scale. Further details on the hydrographic measurements can be found in Fahrbach (1994). Dissolved oxygen was measured with a standard automated Winkler technique with photometric end-point detection, precision 0.2% CV.

Total carbon dioxide (TCO_2 , also known as ΣCO_2 or total Dissolved Inorganic Carbon) is the sum of all inorganic carbon species dissolved in seawater, that is of $[\text{CO}_2]$, $[\text{H}_2\text{CO}_3]$, $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$. Subsamples for the determination of TCO_2 were collected in glass bottles (0.5 l) with inflatable screw caps. Saturated mercury-(II)-chloride was added as a preservative to samples from the upper 250 m. Samples were stored in the dark. All analyses were performed within 24 h, most even within 12 h of sampling. TCO_2 measurements were done by coulometry after Johnson et al. (1985). Coulometer and extraction system were interfaced to a laptop computer (Toplink, TL-3240 V); software for automated data acquisition and operation of sample dispensing and CO_2 extraction was written by M. Stoll (see also Stoll et al., 1993). The precision obtained from all duplicates amounts to $0.85 \mu\text{mol/kg}$. TCO_2 data of the second cruise (ANT X/7) were standard-



used using reference seawater from Dr. A. Dickson of the Scripps Institution of Oceanography (USA). The data of the first cruise, when reference seawater was not yet available, were subsequently standardised with those of the second one in the following way: TCO_2 was plotted vs. potential temperature (θ) for all offshore stations and regression lines were calculated for the temperature range -0.6 to -0.1°C . This range falls within the Weddell Sea Deep Water, TCO_2 values of which are deemed to be seasonally invariable. The ANT X/4 data were corrected such that the θ/TCO_2 relationship was consistent with the ANT X/7 data. This procedure was justified further by comparing the θ/oxygen relationships of both cruises.

Before presenting the data, the impact of freezing and ice formation (and in the opposite case, melting) on salinity, and secondary on other parameters should be addressed. Ice formation, by brine release, increases the surface water salinity, and by freshwater withdrawal also the concentrations of all other dis-

solved species. Different rates of ice formation thus cause spatio-temporal surface variability. If, as in the case of dissolved oxygen, the observed relative variation is an order of magnitude larger than the one of salinity, the contribution of freshwater withdrawal to the overall oxygen variation is less significant. In the case of TCO_2 the relative variation is comparable with that of salinity (both about 1% in the Weddell Sea) and, therefore, a significant part of the observed TCO_2 variation is due to gain or loss of freshwater. We can eliminate this effect by normalising TCO_2 to a common salinity base.

3. Winter surface water

Transects of TCO_2 , dissolved oxygen, temperature and salinity in the surface layer across the Weddell Sea from Kapp Norvegia to the South Orkney Islands are portrayed in Fig. 2. Due to heavy ice conditions the transects have considerable gaps.

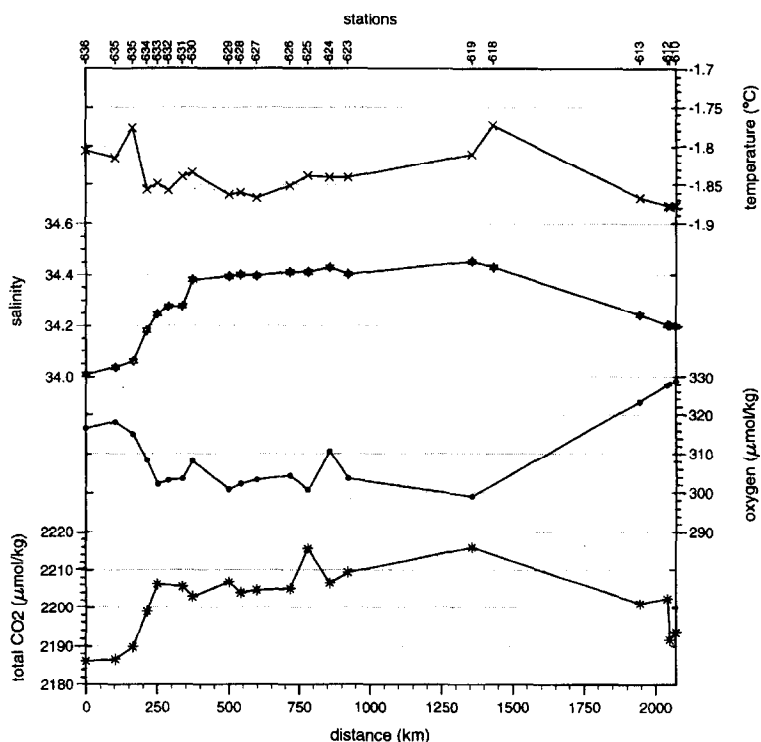


Fig. 2. Surface distribution of TCO_2 , dissolved oxygen, temperature and salinity along the transect from Kapp Norvegia (right) to the South Orkney Islands (left) during the winter cruise.

All properties showed significant variations along the transects. Although the Weddell Sea was nearly fully ice covered and atmospheric temperatures were far below 0°C, the surface layer temperatures were significantly above the freezing point (by up to 0.1°C), apart from stations 610–612 near the continental shelf. This is a clear indication that warmer water from below had been mixed into the surface mixed layer (Gordon and Huber, 1990). In Fig. 3 the same transects as above are shown at the depth of the temperature maximum of the Warm Deep Water. There is a striking similarity between the cross-basin distributions of temperature in the surface and Warm Deep Water layers (the shelf and upper slope station on both sides of the transect excepted; Figs. 2 and 3). This is much less the case for the other properties. The temperature of the surface layer is effected by many processes, and a simple relation between the surface and Warm Deep Water layers is not expected. Still, the resemblance leads one to believe

that the horizontal variation of the surface temperature is brought about through a relatively uniform rate of vertical transport throughout the basin, such that the highest Warm Deep Water temperature causes the highest surface layer temperature.

For salinity the lack of similarity between surface and Warm Deep Water layers was probably due to ice formation or melting in the surface layer. The oxygen minimum in the Warm Deep Water usually coincided with or lay close to the temperature maximum and therefore one would expect a high but inverse lateral correlation of these two properties. That this is not the case results from oxygen depletion in the Warm Deep Water layer through metabolic processes (cf. the Central Intermediate Water; Whitworth and Nowlin, 1987), and from laterally variable air–sea exchanges before the ice cover. The same arguments apply for the TCO₂ distributions, which inversely were quite similar to those of dissolved oxygen (Figs. 2 and 3).

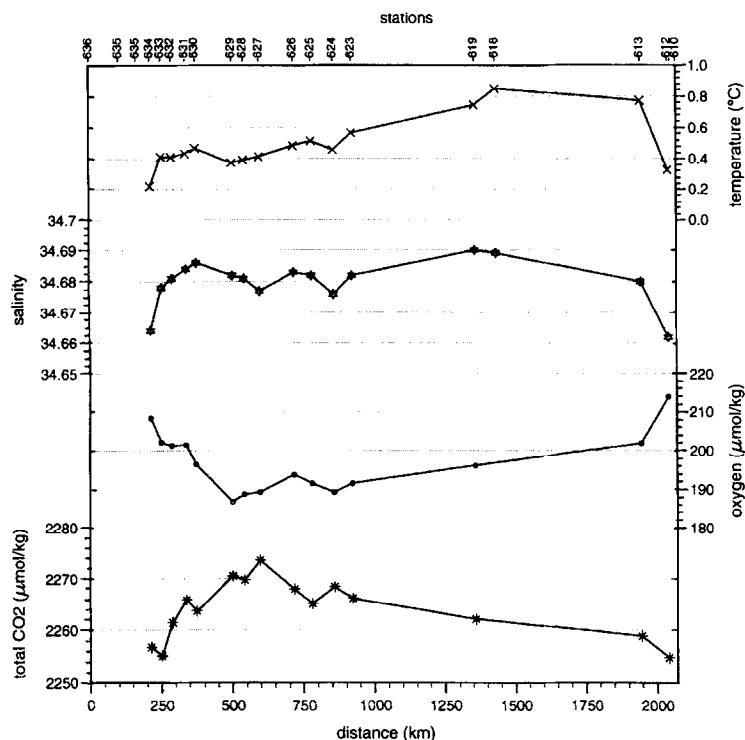


Fig. 3. As in Fig. 2, except at the depth of the temperature maximum. At the stations near the boundaries of the transect no temperature maximum was observed.

3.1. Saturation levels in winter

Our oxygen data display undersaturation of the surface layer all through the basin (Fig. 4). TCO₂ cannot be related to its atmospheric counterpart straightforwardly, to achieve this one needs the partial pressure of CO₂ ($p\text{CO}_2$). This parameter can be calculated from TCO₂ and alkalinity, the latter of which is reported to be conservative in the Weddell Sea (Poisson and Chen, 1987; Anderson et al., 1991). With a normalised alkalinity of $2387 \pm 7 \mu\text{eq/kg}$ at a salinity of 35 (Anderson et al., 1991) and correcting total alkalinity for minor nutrient contributions, a $p\text{CO}_2$ range of 305–331 μatm in the Weddell Sea surface was calculated (Fig. 4); dissociation constants for carbonic acid were taken from Goyet and Poisson (1989). The uncertainty in alkalinity of 7 $\mu\text{eq/kg}$ causes an uncertainty in $p\text{CO}_2$ of 13 μatm . The atmospheric $p\text{CO}_2$ in 1992 being 355 μatm (Siegenthaler and Sarmiento, 1993) this translates into a saturation range of 86–93% with respect to

atmospheric CO₂. This calculated saturation level of CO₂ appears to be higher than that of oxygen.

Undersaturation of oxygen under the sea ice has been observed before in the wintertime Weddell Sea near the prime meridian. It is caused by the admixture of the oxygen-poor Warm Deep Water into the surface layer through entrainment (Gordon and Huber, 1990). Undersaturation of CO₂ under the sea-ice is not obvious. Contrary to oxygen, admixture of Warm Deep Water, in which TCO₂ has a maximum, will increase TCO₂ (and $p\text{CO}_2$) in the surface layer. The observed undersaturation of CO₂ during winter 1992 suggests that at the start of the sea-ice cover the degree of saturation in the surface was probably even less than 86–93%. CO₂ undersaturation is thus preconditioned prior to sea-ice formation. Obviously, rather rapid cooling of the surface layer must have taken place during austral autumn to cause undersaturation of both oxygen and CO₂. Calculations show that an instantaneous decrease of 2°C, the seasonal sea surface temperature range in the Weddell Sea

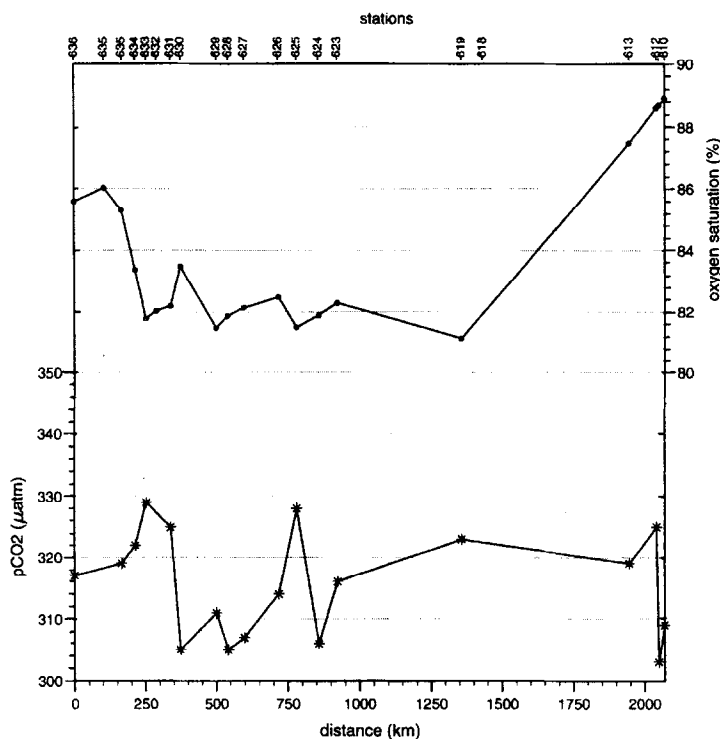


Fig. 4. As in Fig. 2, except for the calculated partial pressure of CO₂ ($p\text{CO}_2$) and the oxygen saturation.

interior being up to 4°C, could indeed bring about a $p\text{CO}_2$ decrease of more than 30 μatm .

For early spring, when the water was still near freezing point and thus with conditions comparable as in the present study, CO_2 undersaturation in the Weddell Sea was reported by Takahashi and Chipman (1982). However, also CO_2 supersaturation has been reported for the spring/wintertime Weddell Sea (Weiss, 1987; Bakker et al., 1995). Apparently, the processes affecting the saturation level of CO_2 in the Weddell Sea are variable. The oxygen saturation level was higher in the eastern shelf/slope area (stations 610–613) than in the offshore Weddell Sea (Fig. 4). This difference is partly caused by more intense ventilation of the water along the continent due to the frequently observed coastal polynya which had also been present during winter 1992 (Haas et al., 1992), and partly to the much larger volume of surface water into which the Warm Deep Water is entrained. The degree of saturation of both oxygen and CO_2 during ANT X/4 in the eastern shelf area

is in perfect agreement with the values presented by Anderson et al. (1991) for the water on the southwestern continental shelves. The remarkable agreement suggests that the saturation level of gases in shelf waters during winter is spatially rather invariant. Furthermore, the significantly different concentrations of dissolved gases in the shelf waters in winter and summer (see Section 4 below) requires that bottom water formation occurs mainly in winter.

4. Summer surface water

Surface distributions of TCO_2 , dissolved oxygen, temperature and salinity across the Weddell Sea from Kapp Norvegia to Joinville Island in austral summer 1992/1993 are shown in Fig. 5. The part of the transect with stations 44–54 coincides with the winter part covering stations 623–629. The variations of all surface properties were much larger in summer than in winter. Important factors in this are

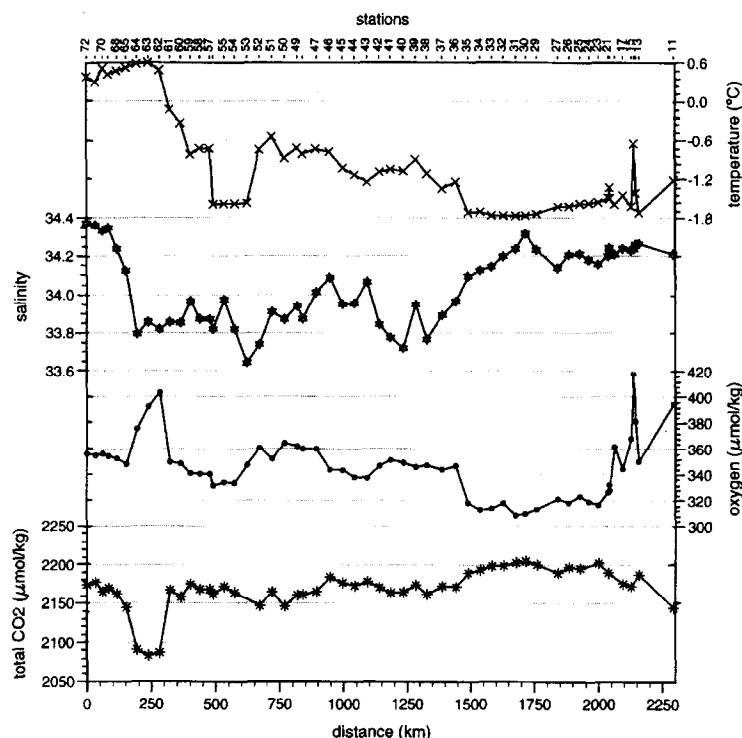
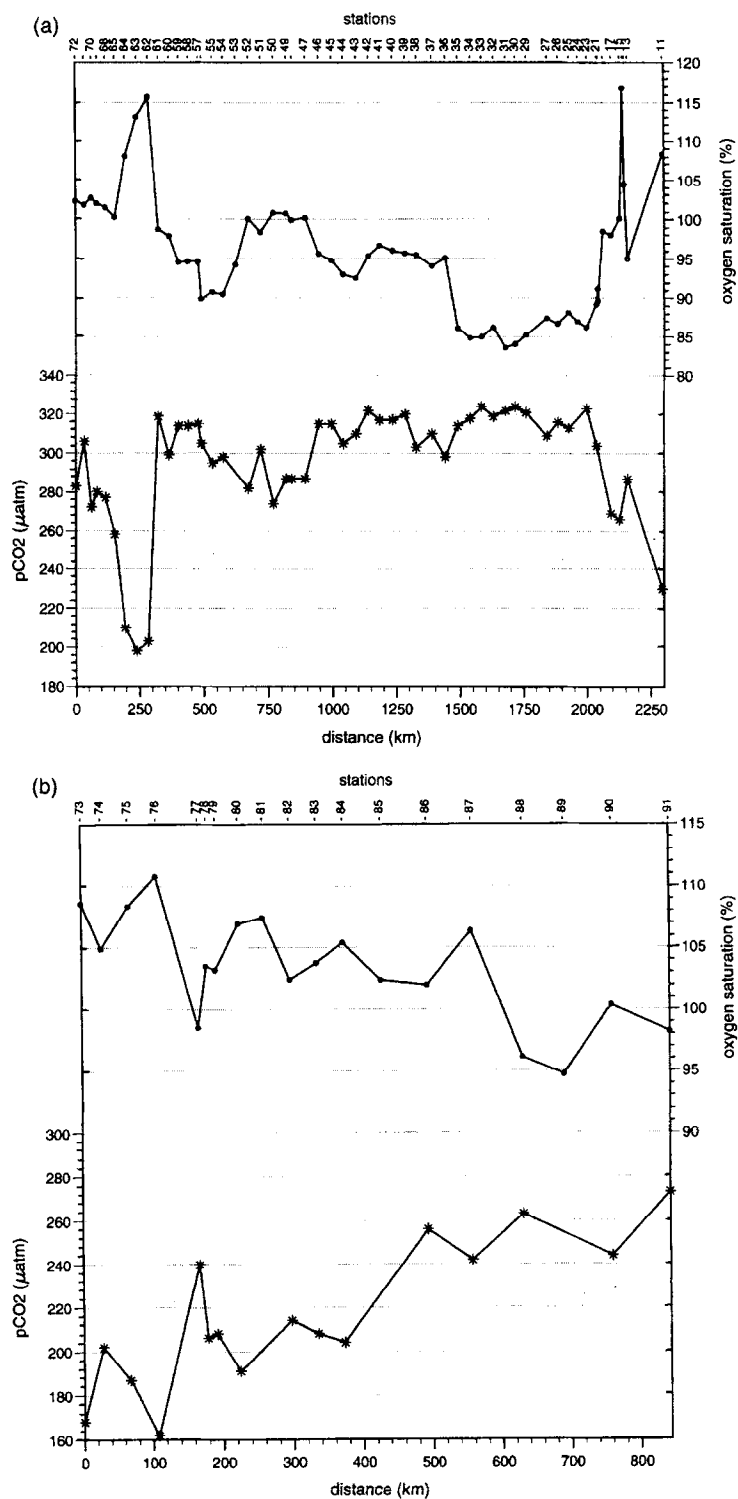


Fig. 5. Surface distribution of TCO_2 , dissolved oxygen, temperature and salinity along the transect from Kapp Norvegia (right) to Joinville Island (left) during the summer cruise.



the lack of ice cover and the increased solar radiation which allowed a significant heat gain of the surface layer. Variation in the surface is subsequently imposed by spatially variable intensity of these factors. Also entrainment of Warm Deep Water due to wind stirring could contribute to the heat gain. Salinity variations were obviously caused by spatio-temporal variations in the melting of the ice pack and advection of melt water. The distributions of dissolved oxygen and TCO_2 result from entrainment of Warm Deep Water during the previous winter and the exchange of these gases between ocean and atmosphere which counteracts the disequilibrium between both reservoirs after the ice started to melt. Furthermore, in late winter and spring phytoplankton primary productivity (Kottmeier and Sullivan, 1987) produces oxygen and consumes CO_2 . All of these processes occur with different intensity in the different areas and moreover closely interact with each other. For instance, increasing stability due to near surface warming and meltwater input is likely to enhance biological activity. In the next sections our observations will be related to these processes.

4.1. Saturation levels in summer

The summer TCO_2 data were transposed into $p\text{CO}_2$ values using the conservativeness of alkalinity. The calculated $p\text{CO}_2$ values (Fig. 6) reveal that, like in winter, the entire Weddell Sea was undersaturated with respect to the atmosphere. The difference with the winter situation is that in some areas the saturation level was much lower. Supersaturation in oxygen occurred only locally (Fig. 6). In the same regions where $p\text{CO}_2$ was far below winter level, oxygen saturation was enhanced compared to the mean winter value of about 82%, suggesting that biological production had occurred. Only after a prolonged period of photosynthesis would oxygen attain supersaturation. On stations 29–35 the $p\text{CO}_2$ and oxygen saturation were only slightly different from the typical winter values (Fig. 4), evidencing that little vertical transport or biological activity had occurred since the winter cruise.

On the Larsen transect extreme conditions were encountered. The very low $p\text{CO}_2$ and the high oxygen saturation suggest abundant photosynthesis previous to our measurements. Closest to the coastline at stations 73–76 this was most pronounced. Further offshore on this transect the lowest salinity of the entire cruise was observed (not shown here; see Fahrbach, 1994), indicating that substantial melting had occurred in this area and south of it. As this melting occurred before the ice cover opened to a large extent, heat must have been supplied by entrainment of Warm Deep Water south of our transect. The relatively low surface temperatures suggest that all heat was used for ice melting and that no heat was available for warming up the surface water. However, the low temperature does not retard the development of the pelagic plankton community, since the low $p\text{CO}_2$ and supersaturation of oxygen attest of intense primary productivity. The low surface salinity, which induces a relatively strong halocline, stabilises the upper water column, thus enabling a bloom to develop. These findings confirm the notion that not temperature as such is the pivotal factor for the start of algal growth (e.g. De Baar, 1994), but rather the stability of the upper water column.

On the main transect, the stations 62–64 displayed the effects of a profound local bloom, and so did station 14 (Fig. 6). This is corroborated by biological measurements (Baumann et al., 1994). On all of these stations the temperature was high (Fig. 5). Between station 65 and the coastline high surface temperatures were observed as well, but in the saturation level of oxygen and the $p\text{CO}_2$ no remainders of a bloom could be tracked.

4.2. Correlations with temperature

Through the availability of light and the stabilisation of the water column the onset of phytoplankton blooms is linked to the pack-ice retreat in spring and summer (e.g. Tréguer and Jacques, 1992). This retreat in turn depends on local meteorological and hydrographic conditions. Sea surface temperature re-

Fig. 6. Surface distribution of $p\text{CO}_2$ and oxygen saturation along the transects from Kapp Norvegia to the Joinville Island (a) and off the Larsen Shelf (b) during the summer cruise.

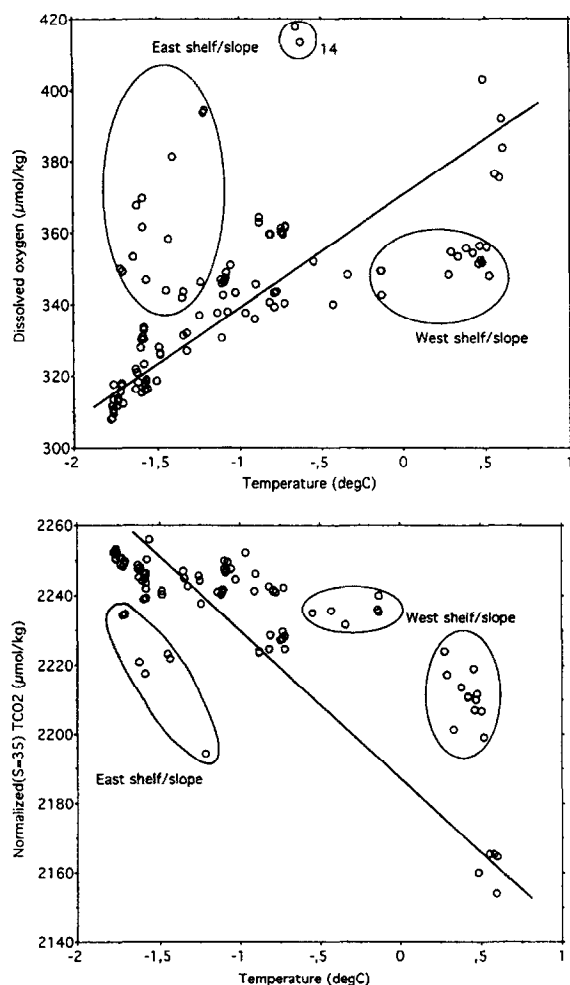


Fig. 7. Dissolved oxygen (top) and normalised TCO₂ (bottom) vs. temperature in the upper 15 m of the water column. Samples of the main summer transect (stations 11–72). The line is hand-drawn. Marked are data from the eastern and western boundary regions.

flects to a large extent the state of the system, which results in a high degree of correspondence between the distributions of dissolved oxygen, TCO₂ and temperature (Fig. 5). In the boundary regions this correlation was less clear. TCO₂ roughly had the inverse shape of temperature and oxygen, but the resemblance is somewhat less because TCO₂ also varies along with the salinity.

In the scatter plots of temperature against dissolved oxygen and normalised ($S = 35$) TCO₂ three different regimes can be distinguished (Fig. 7). In the central region there was a general decrease of TCO₂

and increase of oxygen with increasing temperature, whereas the stations from the eastern and western areas did not comply with this trend. They displayed rather similar concentrations of oxygen and TCO₂ which were in the centre of the observed range, but in the east the temperatures were too low and in the west too high relative to the general trend. This feature can be explained by the different meteorological and hydrographic conditions in the eastern and western boundary regions. Whereas in the east cold air from the continent is even supplied in spring, the Antarctic Peninsula gives rise to a flow of relatively warm air masses into the northwestern Weddell Sea. This difference is also reflected in the sea surface temperatures in the respective areas. Additionally, the rather narrow shelf in the east allows intensive contact of the shelf water with the shelf ice, while this is not the case on the much broader western shelf. Therefore, the contact with the shelf ice in the east leads to melting maintaining the water temperature low in spite of the polynya. In contrast to that, as there is no additional heat sink on the western shelf but a significant flow of Warm Deep Water onto the shelf (Fahrbach et al., 1995), the temperature is relatively high. This scenario is consistent with the salinity distribution, where the salinity in the eastern boundary region is relatively low due to glacial melt water, whereas it is relatively high in the western boundary region due to inflow of Warm Deep Water.

5. Balance calculations

5.1. Estimate of vertical transport

Vertical transport in the central part of the Weddell Gyre occurs by two mechanisms. The divergent Ekman transport due to the transition from westerlies to easterlies induces upwelling in the interior of the gyre, which is apparent as doming of isolines (Mackintosh, 1972). The intensity of this large-scale upwelling varies due to the varying wind fields but it persists all year round due to the stability of the large-scale atmospheric pressure distribution (Taljaard et al., 1969; Gordon et al., 1981). As the vertical velocity vanishes at the sea surface, Ekman pumping affects only transports into the Ekman layer.

The transport into the mixed layer to the surface is effected by entrainment (Gordon and Huber, 1990). It is induced by turbulence, i.e. by wind in the open or ice covered ocean, by thermohaline convection or by relative ice motion. Therefore, entrainment is subject to the variation of the atmospheric forcing as well, which mainly affects its intensity. As entrainment can only effectuate transports across the bottom of the mixed layer if there is enough supply from below, upwelling and entrainment are closely linked.

From the differences between winter and summer measurements on the same about 400 km long transect in the central Weddell Sea (Fig. 1) we can deduce the (late-winter) entrainment of Warm Deep Water into the surface mixed layer. In summer the surface layer is limited to below by a temperature minimum at about 50–125 m depth. As Mosby (1934) already noticed, the temperature minimum is a remnant of the winter surface mixed layer, i.e. it contains mere Winter Water. In the central Weddell Sea the temperature minimum was about 0.1°C above freezing point, which is quite close to the actual winter surface temperature (Fig. 2). The other property profiles did not show an extremum in the temperature minimum layer, but only a gradient change forming an inflection point. This remnant of the winter surface mixed layer can be used to assess the vertical transport, if assumed that all changes between Winter Water and the summer temperature minimum layer are caused by admixture of Warm Deep Water across the thermocline. The shape of the observed temperature minimum, being relatively flat and having a thickness of more than 30 m, indicates that the layer has only been little affected by diffusion and turbulence from above or below. Biology is neither expected to have changed the layer because

the relationships between temperature and dissolved oxygen/ TCO_2 (Fig. 7) suggest that near freezing point biological processes have just not yet started.

For the winter–summer comparison we have chosen two groups of stations, 626–629 (winter) and 49–52 (summer), in a laterally homogeneous area in the central gyre. Table 1 presents surface mean temperature, salinity, TCO_2 and dissolved oxygen of the two groups. In addition, the mean property values are given at the depth of the temperature maximum related to the Warm Deep Water. By a simple calculation the fractions of winter surface water and Warm Deep Water are determined, needed to account for the concentration in the summer temperature minimum layer, the boundary condition being that fraction winter surface water plus fraction Warm Deep Water equals 1. The independent calculations of the fraction of Warm Deep Water that entered the surface mixed layer show a fairly consistent picture for the different parameters (Table 2), with TCO_2 and salinity rendering somewhat higher values than oxygen. Uncertainties result from different shapes of the vertical profiles in the pycnocline/Warm Deep Water range (the dissolved oxygen minimum generally lies shallower than the TCO_2 – and the salinity maxima) and sampling bias.

In order to obtain an entrainment rate we need the time period in which entrainment has been active. Simply taking the time elapsed between our winter and summer cruises (about 5 1/2 months) would yield a rate of $0.133 \times 100 \text{ m} \div 5 \text{ 1/2 months} =$ about 2.4 m/month (where 100 m is the winter mixed layer depth and 0.133 the calculated fraction of entrained WDW). This is rather low compared with the entrainment rates given by Gordon and Huber (1990). A better estimate of the time span in

Table 1

Dissolved gases and hydrographic data for different summer (stations 49–52) and winter (stations 626–629) surface strata and for the mean (summer and winter combined) temperature maximum layer. Error bars represent one standard deviation

	TCO_2 ($\mu\text{mol/kg}$)	Oxygen ($\mu\text{mol/kg}$)	Temperature (°C)	Salinity
Winter surface	2205.4 ± 0.9	302.6 ± 0.9	-1.861 ± 0.003	34.404 ± 0.004
Summer temperature minimum	2217.4 ± 0.6	287.5 ± 1.2	-1.785 ± 0.018	34.447 ± 0.006
Summer surface	2193.4 ± 3.6	321.3 ± 5.0	-0.726 ± 0.112^a	34.252 ± 0.051
WDW temperature maximum	2269.2 ± 0.7	189.2 ± 0.5	0.422 ± 0.024	34.682 ± 0.001

^a Upper 10 m of water column.

Table 2

Fractions (%) of Warm Deep Water entrained into the winter surface water between July 1992 and January 1993 calculated with the data from Table 1 using three different properties

	Fraction WDW	Fraction winter surface water
TCO ₂	18.8 ± 2.8	81.2 ± 2.8
Oxygen	13.3 ± 2.0	86.7 ± 2.0
Salinity	15.5 ± 2.4	84.5 ± 2.4

which vigorous entrainment is active is deduced from observations of drifter buoys equipped with an air temperature sensor and a thermistor chain in the water (Sellmann and Kottmeier, 1993). Air temperature rose precipitously after the beginning of October yielding an entrainment period of three months since the winter cruise. These data would render an entrainment rate of about 4.4 m/month. If we assume that entrainment outside the period of ice cover is only small, the late-winter entrainment rate in the central Weddell Gyre is close to 4–5 m/month. During the entire 7 month period of ice cover (Anonymous, 1985) this would yield a total entrainment of about 30 m. This value is on the low end of the range calculated by Gordon and Huber (1990). An explanation for this discrepancy is that the late-winter entrainment is less intensive than the entrainment accompanying closure of the ice blanket when intense heat losses generate intensive turbulence.

5.2. Surface balance of carbon dioxide and oxygen

Between the winter and summer cruises the concentrations of carbon dioxide and oxygen in the surface layer were modified mainly by vertical transport, photosynthesis and air–sea exchange. Photosynthesis activity can be obtained indirectly by comparing the summer surface layer and the Winter Water remnant. The method will be described here-

after. Then, with the known vertical transport, the atmospheric exchanges of the two gases are simply the closing entry of a balance considering the total changes between the winter surface mixed layer and the summer surface layer.

The development of the summer surface stratification includes melting of the sea ice and warming of the upper part of the original Winter Water layer. The cap of Summer Surface Water and the remnant Winter Water are well separated by the seasonal thermocline. Both originate from the same initial water mass, but air–sea exchange and photosynthesis only occur in the Summer Surface Water. Therefore, comparing these strata gives information about the extent of the processes in the surface layer since the end of winter. Photosynthesis within, or atmospheric supply to the temperature minimum layer would affect the results of the calculations. However, those effects are thought to be minor.

To find the changes in TCO₂ and oxygen due to photosynthesis, the phosphate concentration is taken as a proxy. Phosphate is, like CO₂, removed from the surface compared to the temperature minimum layer due to photosynthesis, but unlike CO₂ and oxygen it is not volatile. The relationship between the phosphate change and TCO₂/oxygen changes is described by the well-known Redfield ratio's (Redfield et al., 1963), saying that $\Delta\text{phosphate}:\Delta\text{TCO}_2:\Delta\text{oxygen} = 1:106:-138$ (molar). Considering the nutrient data collected during the summer cruise these classical ratio's basically seem to be pertinent to the surface layer. The mean depletion of phosphate (stations 49–52) in the surface layer compared with the temperature minimum layer was $0.134 \pm 0.026 \mu\text{mol/kg}$ (phosphate data, courtesy K.-U. Richter, Alfred-Wegener-Institut). This value for phosphate, as all other property values of the summer surface layer (Table 1) is a weighted average over the water column above the

Table 3

Balance of changes in dissolved gases ($\mu\text{mol/kg}$) between the winter mixed layer (July) and the summer surface layer (next January) shallower than the temperature minimum. Confidence intervals are a combination of error propagation and estimated additional uncertainties

	Vertical transport	+	Biology	+	Atmosphere	=	Total
TCO ₂	+ 8.5 (± 2.6)		– 13.9 (± 5.0)		+ 3.1 (± 3.1)		– 2.3 (± 4.5)
Oxygen	– 15.1 (± 4.6)		+ 18.5 (± 6.0)		+ 13.3 (± 7.3)		+ 16.7 (± 5.9)

temperature minimum because sharp gradients occur in the surface layer.

The changes in TCO_2 and oxygen due to biological processes calculated using the Redfield ratio's appear in Table 3, together with all other budget entries. Vertical transports were calculated using the oxygen-derived Warm Deep Water fraction which is thought to be most reliable (Section 5.1). The total changes between the winter surface mixed layer and the summer surface layer were taken from Table 1. It should be noted that the real decrease of TCO_2 from winter to summer was much larger than the figure that appears in the balance (Table 3) because the major part of this decrease is simply due to dilution, which is illustrated by the related salinity decrease. Therefore, the total change is the normalised difference.

The confidence intervals are partly calculated and partly estimated. Inevitably, the confidence intervals in a balance like this are rather large, but still the balance illustrates well the relative importance of the different contributors to changes in the surface layer. Despite being active only during a short period of the total balance time span, biological processes appear to be the largest entry for both dissolved gases. During the rest of the summer primary productivity will continue, thereby further raising the oxygen and TCO_2 entries in magnitude. Of course the atmospheric entry will change accordingly then.

The present balance only represents an arbitrary timing between winter and this early stage of summer. Still, it indicates that the changes caused by vertical transports during winter did not cause additional outgassing of CO_2 to the atmosphere in spring. Remarkably, both oxygen and CO_2 were absorbed from the atmosphere despite their generally opposite tendencies in biological processes. For oxygen the reason is that after the opening of the ice blanket, the water, which was substantially undersaturated due to previous vertical transport of oxygen-poor Warm Deep Water, was partly replenished. For CO_2 the undersaturation after opening of the ice cover was much less. Therefore, and also due to the slow equilibration time of CO_2 , the invasion of atmospheric CO_2 was mainly the consequence of the uptake of CO_2 in the surface water by the phytoplankton. This also compensated the CO_2 increase due to vertical transport.

6. Discussion and conclusions

The calculated undersaturation of $p\text{CO}_2$ in winter is surprising indeed. Supersaturation was perhaps expected because of Warm Deep Water entrainment into the surface layer, which increases the latter's CO_2 content. Differences between measured and calculated $p\text{CO}_2$ values amounting to up to $30 \mu\text{atm}$ have been reported (e.g. Metzl et al., 1991), with calculated values tending to be on the low side. An explanation for this difference is not at hand. Using different sets of dissociation constants of carbonic acid could change the picture to some extent, especially at low temperatures (see Goyet et al., 1991, fig. 3). Measured $p\text{CO}_2$ data should be considered more reliable. This discrepancy, however, does not have influence on the results and conclusions inferred from the balance calculations, since these are only dependent on the measured TCO_2 .

That vertical transport of Warm Deep Water leads to an enhancement of the TCO_2 and $p\text{CO}_2$ of the surface water of the Weddell Sea has been well-known (Weiss et al., 1979; Chen, 1982). Previous investigators concluded that because of this the Weddell Sea is a source of CO_2 in winter (Takahashi et al., 1993). This vertical transport has been one of the main reasons to disregard the Antarctic Ocean as an effective sink for (excess) atmospheric CO_2 , in contrast with the North Atlantic Ocean, the other high latitude area where net cooling of surface waters takes place. The present study indicates that during autumn cooling the Weddell Sea will probably be a sink for atmospheric CO_2 . During winter the Weddell Sea is almost fully ice-covered which largely hampers gas exchanges between the water and the air above. Although in winter vertical transport of CO_2 -rich Warm Deep Water raises the CO_2 content of the surface layer, this is not enough to cause serious outgassing at the end of winter. In spring and early summer CO_2 is taken up from the atmosphere as well (Fig. 6) due to the undersaturation caused by abundant photosynthesis. This is furthermore corroborated by Takahashi et al. (1993) who used the majority of existing CO_2 data. One could state that before physical processes get effective in their drive towards CO_2 supersaturation, biological activity has already reduced the $p\text{CO}_2$ far below full saturation. Unknown are the exact conditions prevailing late

summer and early autumn, although one can speculate about it. Probably, the bulk of remineralisation of organic matter produced in the previous season will take place, invoking the Weddell Sea to become a source of CO_2 . However, not all organic matter will be remineralised in the surface layer, part of the production rains down and is remineralised at depth or reaches the ocean floor. This has been explicitly observed as sizable Total Organic Carbon maxima in the deep Weddell Sea (Wedborg et al., 1995). Thus, all other conditions being equal, during the production period more CO_2 can be taken up from the atmosphere than can be returned to it during the mineralisation period. This is of course the concept that is generally known as the biological pump (Volk and Hoffert, 1985).

Whether on an annual basis the Weddell Sea is a source or sink for CO_2 depends not only on the well-known bottom water formation, but also on the relative importance of upwelling vs. the biological pump. That latter mechanism is meaningful in the Weddell Sea is supported by the TCO_2 distribution in the intermediate and deep water. The greater part of the water column below the Warm Deep Water core contains CO_2 in excess of the expected amount based on conservative mixing between Warm Deep Water and shelf water (Hoppema et al., in prep.). The previously described Central Intermediate Water (Whitworth and Nowlin, 1987) with its oxygen minimum (and TCO_2 maximum) is an extreme expression of this phenomenon. The magnitude of this biologically mediated CO_2 excess is definitely comparable with the amounts of CO_2 involved in the upwelling of Warm Deep Water into the surface layer. In the end, the deep water leaves the Weddell Sea northwards, contributing to the deep and bottom waters of the Antarctic Circumpolar Current. Thus, not only the strength of the biological pump in the Weddell Sea is important, but also the rate of deep water transport out of the Weddell Sea.

Increasing atmospheric CO_2 levels have the effect that the CO_2 content in the Weddell Sea surface layer increases due to air–sea exchange, which in turn decreases the CO_2 difference between the surface water and the Warm Deep Water. This makes the contribution of vertical transport to the surface layer balance relatively less important which will shift the atmospheric entry towards a larger sink (cf.

Table 3). This, in fact, increased uptake of atmospheric CO_2 is, however, a transient phenomenon because the Warm Deep Water will with a delay also become enriched in atmospheric CO_2 .

Enhanced uptake, of anthropogenic CO_2 , in the Weddell Sea via the biological pump mechanism may be feasible. Uptake of anthropogenic CO_2 via the biological pump used to be considered impossible (Smith and Mackenzie, 1991), but recent investigations indicated that due to CO_2 growth limitation there may after all be a relation between atmospheric CO_2 levels and the biological pump (Riebesell et al., 1993). Another (established) way of taking up anthropogenic CO_2 is by way of bottom water formation (Anderson et al., 1991) and possibly by deep water formation. Which of the two ways of anthropogenic CO_2 sequestering is more important in the Weddell Sea remains to be ascertained.

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